SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATIONS OF HYDROTALCITE-TYPE ANIONIC CLAYS

SYNOPSIS

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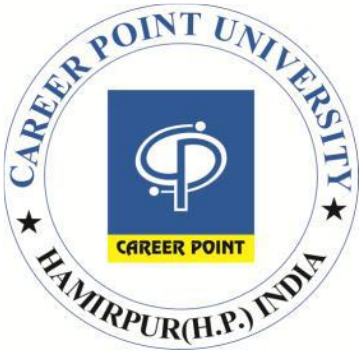

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Introduction

Metals are prevailing in the environment and play significant roles in human life. They are derived both naturally and anthropogenic sources. Metals comprise about 75% of the known elements and can form alloys with each other and with non-metals (Spark et al., 2005). Chemically, metals are defined as elements that conduct electricity, are malleable and ductile, have a metallic lustre, form cations and have basic oxides. Terms generally used in relation to metals in biological and environmental studies are metal, metalloid, semimetal, light metal, heavy metal, beneficial metal, essential metal, toxic metal, trace metal, abundant metal and micronutrients (Ali et al., 2019). Metals are important components of our homes, automobiles, appliances, tools, computers and other electronic devices, and are essential to our infrastructure including highways, bridges, railroads, airports, electrical utilities, and food production and distribution. Certain metals are essential for plant growth, animals and human health. But, if present in excess they become toxic (Spark et al., 2005). Their deficiency or excess can lead to disturbance of metabolism and causes many diseases. They play important physiological and biochemical roles in the body as they may be part of biomolecules such as enzymes, which catalyse biochemical reactions in the body (Ali et al., 2019). Metals have various uses and applications in the industry-dominated society **(Table 1)**.

Table 1. Uses and applications of various metals in different industrial processes and products.

Metal	Uses
Ni	Catalyst and battery manufacturing, nickel coating, nickel stainless steel, catalyst and pigment
Pb	Car batteries, radiation protection, pigments, lead crystal glass, architecture
Zn	Batteries, coating compounds, crops, die casting alloys
Cu	Electrical wiring, stoves, portable CD players, transmission wires, copper alloys and coins
Cd	Electroplating of steel, Ni-Cd batteries, cellular telephones, laptops, computers
Hg	Fluorescent lights, felt production, batteries, thermometers, barometers
As	Rat poisons, bronzing, in forming special glass and preserve wood

Cr	Stainless steel production, electroplating, leather tanning, textile manufacturing, wood preservation
Mn	Oxidising agent, depolariser in dry cells, decolourise glass, to form alloys
Co	Electroplating, magnet steels and stainless steels, paint pigments

Metal ions are effectively used as a green catalyst in the industry. Green or Sustainable Chemistry is a term related to the creation of chemical products and processes that reduce or eliminate the use and production of harmful substances. The twelve principles of green chemistry include prevention, atomic energy, safer chemical synthesis, safer chemical design, use of safer solvents and auxiliaries, use of renewable raw materials, reduction of derivatives, catalysis, degradation products design, real time analysis for pollution prevention and accidents prevention (Ivankovic et al., 2017; de Marco et al., 2018). Catalysis is one of them, which is considered most important for the various reactions. The foundation of green chemistry with new catalytic reactions and new types catalyst combination offers several benefits in terms of process utilization, selectivity, energy reduction and the use of alternative reaction media (Ivankovic et al., 2017).

Catalysis: Catalysis is a pivotal technology that affects our day-to-day life in many ways. Over 90% of all chemical manufacturing is based on catalytic processes (Feng et al., 2015). Commonly, catalysis is defined as the phenomenon of increasing the rate of a chemical reaction in addition to a small quantity of an external substance known as the catalyst. The term catalysis was first introduced in 1836 by Berzelius, a Swedish chemist, but scientifically defined firstly by Ostwald in 1894. The catalysis word originally came from Greek words *kata* (cata) which means down and *lyein* (lysis) means loosen. A catalyst provides an alternative pathway for the reaction by lowering the activation energy barrier. The catalytic reactions are carried out under milder conditions and thus saving the energy as well as produce desired products through a selective route using fewer resources and thus minimize the waste (Bharali, 2017). Catalytic technologies play a key role in the economic development and growth of the chemical industry due to the increasing demand for new and green processes to produce many industrially important chemicals as catalysis has a wide range of applications (Sangeetha, 2007). Catalysis is classified into two major types: homogeneous and heterogeneous catalysis.

Homogeneous catalysis: In this type of catalysis, the catalyst is present in the same phase as the reactant and forms a single phase. For examples, enzyme and acid-base catalysis are considered as the most important homogeneous catalysis (Bharali, 2017). The homogeneous catalyst shows good control over its preparation, high efficiency and selectivity and needs comparatively mild reaction conditions and has uniform nature of catalytically active sites (Mariamma, 2002). The disadvantages of homogeneous catalysts are they may be poisoned and hence its separation from the product in the reusable form is difficult (Sangeetha, 2007). Moreover, high cost, corrosion, toxicity, generation of huge amounts of solid waste products etc. make the homogeneous catalytic reactions environmentally and economically unsuitable for industrial applications (Bharali, 2017). It would be a better choice for chemical industries to choose for heterogeneous catalysts, as they are much less susceptible to poisoning (Sangeetha, 2007).

Heterogeneous Catalysis: In heterogeneous catalysis, the catalyst is present in different phases as that of the reactant and usually these are solid materials. The surface reactions fall into this category. The heterogeneous catalysts have several advantages over homogeneous catalysts. They are easy to separate after the completion of reaction and are economical, have good thermal stability, have multiple active sites and are reusable. In case of solid-gaseous systems, the catalyst can be easily separated and cleaned. In liquid-solid systems, it can be separated simply by filtration. A numerous chemical process has been carried out in industry following catalytic route and major production of bulk chemicals involves the use of solid heterogeneous catalysts. Since, the catalytic reaction occurs at specific surface sites, called active sites, heterogeneous catalysts are often regarded as the surface catalysts. The heterogeneous catalytic reaction involves the following steps:

1. Diffusion of the reactant from its bulk to the surface of the catalyst,
2. Chemisorption of the reactant on the catalyst surface,
3. Chemical reaction on the surface,
4. Desorption of the reaction products from the surface
5. Diffusion of the product molecules from near the surface into the bulk.

Thus, the adsorption is the important step for any heterogeneous catalytic reaction. An alternative sequence of elementary steps can be acquired due to the presence of a catalyst

to obtain the desired product. The efficiency of a heterogeneous catalyst can also be understood in terms of activity and selectivity with morphological characteristics like surface area, active surface sites per unit area and crystallinity. Therefore, heterogeneous catalysts have played a dynamic role in different fields such as production of chemical intermediates, polymers, drug molecules, agrochemicals and packaging materials etc. (Bharali, 2017). Clays, zeolites, mesoporous materials, microporous aluminosilicates and zeotype catalysts such as aluminophosphates have been playing important roles as heterocatalysts in the production of heavy and fine chemicals (Sangeetha, 2007).

Clays: Clays are naturally occurring materials composed primarily of fine-grained minerals and found on the surface of earth composed mainly of silica, alumina, water and weathered rock. These are effectively used as an adsorbent to trace heavy metal ions present in aqueous solutions for more than a decade now. The use of clay as adsorbent has advantages upon many other commercially available adsorbents in terms of low cost, an abundant availability, high specific surface area, excellent adsorption properties, non-toxic nature, and high potential for ion exchange (Uddin, 2017). The two main features that evoke the interest in clays are their common availability and their extraordinary properties. Clays find their potential application in building materials, ceramics, adsorbents, sensors, ion-exchangers, decolorizing agents and catalysis. The adsorptive power and high-water retention capacity of clays is responsible for their wide applications. The first and most widely known application of clay on catalysis is French Houdry cracking process developed in 1930. Clays form a subset of a large discipline of catalysts as heterogeneous catalysts (Churchil, 2011). Clays are classified into two categories:

1. Cationic or Smectite type: These types of clays have layered lattice structure in which two dimensional oxyanions are separated by layers of hydrated cations (Jinesh, 2012). Cationic clays exist in vast quantities in nature and are mainly prepared starting from the minerals and are commonly used for many chemical transformations. One example for cationic clay is commercially modified montmorillonites, K10 or KSF, widely used as acid catalyst or adsorbent in hydrocarbon cracking. Analogously, “Clayfen” and “Claycop” are the acronyms for iron (III) or copper (II) nitrate supported on K10 clay. Cationic clays are mainly obtained from natural materials that invariably contain impurities such as quartz, calcite, feldspars, etc., although they may also be synthesized, for example laponite1 (Sangeetha, 2007).

2. Anionic or Brucite type: These types of clays have charge on the layer and the gallery anion is reversed, complementary to cationic clays (Jinesh, 2012). Anionic clays may be defined by their chemical composition, basal spacing and stacking sequence. Hydrotalcites belong to the class of anionic clays and are natural or synthetic lamellar mixed hydroxides with interlayer spaces containing exchangeable anions and different names are used depending on the composition and polytype form. Anionic clays are usually synthesized by precipitation methods and are widely used as industrial adsorbents, ion exchangers and scavengers in industry and laboratory producing regio- and stereo-selective processes. Hydrotalcite-like materials based on anionic clays have produced sensational success in many organic syntheses in recent years and represent a puzzle catalyst in many more reactions (Sangeetha, 2007).

Hydrotalcite: Hydrotalcite (HT) is magnesium/aluminium hydroxyl carbonate layered material which can be easily crushed into white powder was first discovered in Sweden in 1842. The stoichiometry of hydrotalcite, $[Mg_6Al_2(OH)_2]CO_3.4H2O$, was first correctly determined by Manasse in 1915, who was also the first to recognize that carbonate ions were essential for its structure. In 1930 Aminoff and Broome recognized the existence of two polytypes of HTs with rhombohedral and hexagonal symmetry (proposed by Manasse) through X-ray investigation (Churchil, 2011). In 1942, through the synthesis of large number of compounds of HT-like structures, Feitknecht proposed that the structure was assumed to be exist of consecutive layers of brucite [$Mg(OH)_2$], and aluminium hydroxide [$Al(OH)_3$] and gave the name double sheet structures (Jinesh, 2012). In 1969, Allmann and Taylor showed that all the cations were in the same layer, and anions together with water molecules lie in the interlayer region through single crystal X-ray diffraction (XRD). The first patent on HT as catalyst came in 1970 as an optimal precursor for the preparation of hydrogenation catalysts. Nearly 40 years later, still many of the fine details of the structure such as the range of possible compositions and stoichiometry, the extent of ordering of metal cations within the layers, the stacking arrangements of the layers, the arrangement of the anions and water molecules in the interlayer galleries are not fully understood (Churchil,2011). A literature search of layered materials, over the period of 2000-2006, revealed nearly 20,000 papers which includes layered perovskites (LP), pillared clays (PILC) and layered double hydroxides (LDH) materials, of which about 85% were dealing on catalysis. It is also evidenced from the literature that the similar layered hydroxides like layered perovskites (LP) and pillared clays (PILC) materials are still

mainly at the lab-scale development stage, while hydrotalcites find a broad range of applications. This shows the importance of working on clays and clay-based compounds. Hydrotalcites constitute a class of extremely useful materials for scientists especially in fields like catalysis, and ion-exchange (Jinesh, 2012).

Structure: Hydrotalcite (HT) compounds are also known as double layered hydroxide, have a structure similar to the brucite Mg $(OH)_2$, where the Mg^{2+} cations are bonded to the six OH^- anions, forming an octahedral arrangement (Barbosa et al., 2017; Shamsudin et al., 2013). Both the layers constituted of localized cations where M^{2+} cations are substituted by M^{3+} cations and interlayers containing the charge balancing anions and water molecules. These consist of hydroxyl ions held together by van der Waal's force. When a fraction of Mg^{2+} ions in the brucite is substituted by trivalent cations such as Al^{3+}, hydroxide layers exhibit anionic mobility, anion exchange and sorption properties in addition to surface basicity. These properties make HT highly potential for base-catalysed reactions (Shamsudin et al., 2013). Hydrotalcite-like compounds are referred to anionic clays in comparison with cationic clays and are an important class of ionic lamellar solids (Sahu, 2016). The general formula of LDHs materials is:

$$[M^{2+}_{1-x} M^{3+}_{x} (OH)_2 (An-)_{x/n}] \cdot yH_2O$$

Where

a) M^{2+} = divalent cation (Mg^{2+}, Ca^{2+}, Zn^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, etc.).

b) M^{3+} = trivalent cation (Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Mn^{3+} etc.).

c) An- = interlayer anion with charge n- (Cl^-, CO_3^{2-}, NO_3^-, OH^- etc.).

d) x represents the molar ratio of [M (III) / (M (II) + M (III))]; and x is normally between 0.17 and 0.33.

e) y = number of water molecules located in the interlayer space (Grosu et al., 2018; Sahu, 2016; Saikia and Goswamee, 2018; Benicioa et al., 2018).

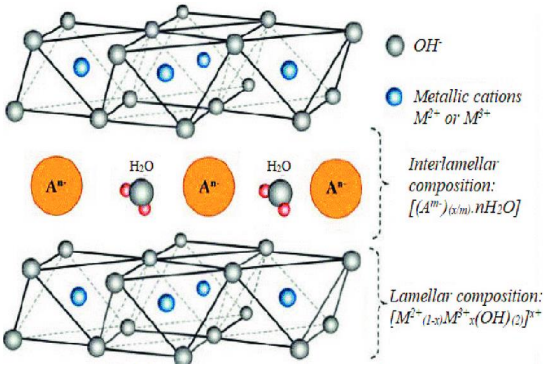

Fig 1: General structure of hydrotalcite (Arruda et al., 2013).

Generally, activation of HT involves a heat treatment wherein the layered structure is destroyed to form a mixed oxide. In a next step the material is rehydrated to restore the original HT structure to a large extent and with the exclusion of other anions and CO_2, Bronsted base sites (H_2O) are incorporated in the interlayer (Karthikeyan and Manivannan, 2015).

Synthesis: There are various methods for the synthesis of hydrotalcite-like materials like co-precipitation, ion exchange, hydrothermal synthesis, sol-gel synthesis, reconstruction (Bini and Monteforte, 2018) but most commonly used method is co-precipitation (Babakhani et al., 2014; Lin et al., 2017; Wiyantokoa et al., 2015; Shekoohi et al., 2017; Benicioa et al., 2018). Co-precipitation is done in two different forms: co-precipitation at variable pH and co-precipitation at constant pH (Shekoohi et al., 2017). In the variable pH method, a solution containing salts of the divalent and trivalent cations is added to an alkaline solution containing the anion that will be interleaved (Arruda et al., 2013). In the co-precipitation at constant pH approach, divalent and trivalent cation salt solutions, the anion to be intercalated and alkaline solution, all are mixed at the same time (Shekoohi et al., 2017). The pH of the mixture is maintained to the optimal basic value (pH range 6-11) (Bini and Monteforte, 2018).

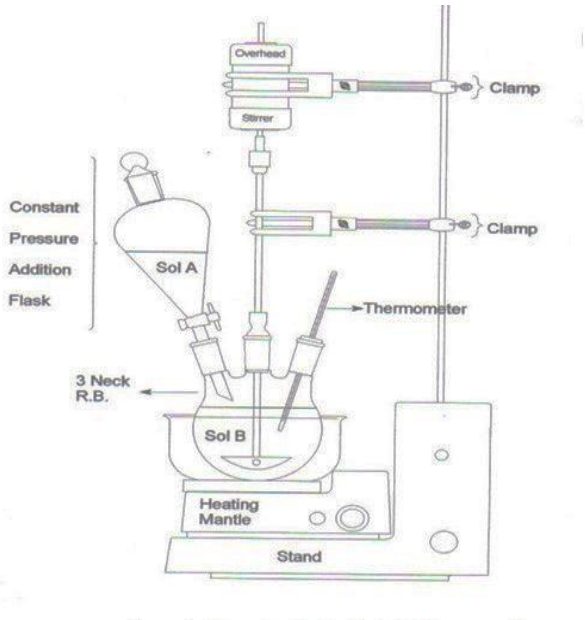

Fig 2: The set up for the hydrotalcite preparation (Bhat, 2012)

The co-precipitation at constant method requires the use of a more sophisticated experimental apparatus, but it results in particles with greater uniformity. As pH is

increased, the cation reacts with OH- and CO_3^{2-} generating hydrotalcite, which has very low solubility and therefore precipitates (Arruda et al., 2013). These reactions are performed under strong stirring and require a further purification step to remove any remaining counter ions (Shekoohi et al., 2017). In addition to the reactant's concentrations, the speed of addition, the final pH of the suspension, the degree of agitation (usually vigorous) and the mixture temperature must be carefully controlled. Co-precipitation is usually carried out at relatively low temperatures (up to only 35°C) to prevent the formation of other phases such as simple hydroxides (Arruda et al., 2013). In the synthesis of nanostructure hydrotalcite, the size and shape of the nanoparticles can also be controlled by pH, temperature, type of salt and their ionic strength, as well as ratio of the metal cations. Moreover, the increase in mixing rate tends to decrease the particle size (Shekoohi et al., 2017). So, hydrotalcite-like materials show a number of applications and are easy to synthesize.

Properties: Hydrotalcite-type anionic clays (HTs) are increasingly regarded as a good alternative to the traditional homogenous base catalysts such as NaOH and KOH for several base-catalysed reactions (Sahu, 2017) that are important for the cosmetic (Bastianini et al., 2018) and pharmaceutical industries (Al-blewi et al., 2018), electrode modifiers for supercapacitors (Yan et al., 2018; Xiao et al., 2018; Liu et al., 2019). The main property of hydrotalcites is their anion exchange capacity, which makes them unique inorganic materials to intercalate organic or inorganic anion (Sahu, 2016). The variety of applications of hydrotalcite based materials is virtually unlimited. Hydrotalcites can be used in the preparation of catalysts for the production of H_2 (Laine et al., 2018), preparation of organic compounds (Sahu, 2017; Sahu et al., 2018) and production of biodiesel by trans-esterification of triglycerides with methanol (Karthikeyan and Manivannan, 2014). These are used in the green synthesis of various compounds (Sahu, 2016; 2017). Because of the large surface area and regeneration ability, LDHs are used as adsorbents for purification of wastewater (Ayawei et al., 2017), removal of fluoride (Wang and He, 2014), chromium (Qabaqous et al., 2018), arsenic (Wang et al., 2018), lead (Haraldy et al., 2019), technetium (Rashad and Someda, 2015) ions from water. These are effectively used in the degradation of PET (Polyethylene terephthalate) bottles (Sharma et al., 2012; 2015) and in agriculture (Benicioa et al., 2018). Besides these, hydrotalcites are also used in preparation of flame-retardant paper (Wang et al., 2012), packaging material (Cheng et al., 2019; Barik and Badamali, 2017). In addition to the above, numerous experimental investigations have

been published on the use of hydrotalcites for catalytic applications (Afi et al., 2018; Valverde et al., 2014; Sahu et al., 2018; Hamlich et al., 2017; Nguyen et al., 2018, Li et al., 2019; Yan et al. 2017; Coumans et al., 2018; Gupta et al., 2017). In the concern of green chemistry, hydrotalcite-type anionic clays provide several advantages over corrosive catalysts like recycling, easy separation from the reaction mixture and high surface area which increases their catalytic activity. Because of the association of the various primacy factors with HTs, they attracted considerable attention from chemists for their use in the field of organic synthesis.

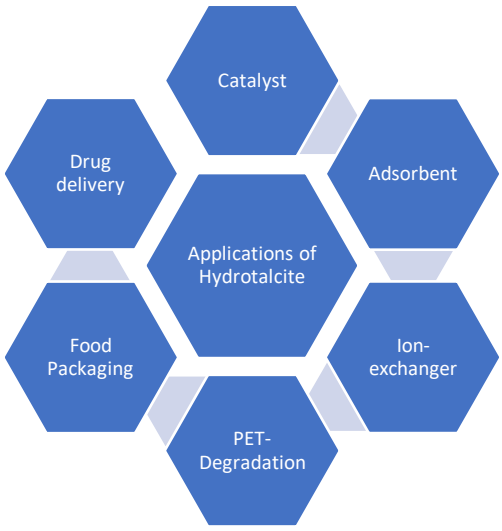

Fig 3: Applications of Hydrotalcite-type anionic clays.

Literature Review

Hydrotalcite-type anionic clays have been used as innovative research materials for a long time. Numerous researches have been reported on synthesis and applications of the hydrotalcite like materials.

Mariamma in 2002 had reported the surface acidity/basicity of rare earth metal-aluminium mixed oxide catalysts. The oxides prepared by precipitation method and their surface acidic and basic properties vary with temperature of activation, method of preparation and other pre-treatment techniques.

In 2005, Spark et al. studied the toxic metals in the environment, the role of surfaces. They found that if the metals present in excessive concentrations, they became toxic and metals underwent an array of biogeochemical processes at reactive natural surfaces.

Sangeetha in 2007 had reported the hydrotalcite supported Pd-catalysts for hydrogenation, dehydrogenation and combination reactions and hydrotalcite supported palladium catalyst found to be a highly active catalyst for these reactions as a highly active base catalyst.

Churchil in 2011 had carried out a structure property relationship study of LDHs and studied the variations of synthesis methodologies and their influence on catalytic behaviour and synthesised dihydropyridines (DHP) at room temperature using LDHs as environmentally friendly solid base catalyst.

In 2012, Sharma et al. had reported the recycling of waste Polyethylene terephthalate (PET)-bottles using dimethyl sulfoxide (DMSO) and hydrotalcite catalyst. Hydrotalcite in presence of DMSO as a solvent could degrade PET to dimethyl terephthalate (DMT) and ethylene glycol (EG) could be used as recyclable catalyst.

Wang et al. in 2012 had carried out a study on Mg-Al hydrotalcites in flame retardant paper preparation. They found that Mg-al hydrotalcites adversely affected the physical strength of flame-retardant paper and played the role of filling and whitening.

Jinesh in 2012 had reported the catalytic and ion-exchange applications of hydrotalcite-like materials. LDHs materials showed the dual advantage in environmental perspective in both for remediation of chromate and utilization of thus derived material as selective oxidation catalyst.

Bhat in 2012 studied the synthesis and characterization of hydrotalcite and hydrotalcite compounds and their applications as a base catalyst for aldol condensation reaction. He reported that the Mg-Al hydrotalcite catalysed aldol reaction propionaldehyde conversion of 57.78% and with selectivity 51.23% to methacrolein.

Arruda et al. in 2013 had carried out a study on hydrotalcite ($Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$), a potentially useful raw material for refractories. They confirmed that Mg-Al hydrotalcite is a potentially useful raw material for refractories.

In 2013, Shamsudin et al. described glycine as an alternative fuel in making hydrotalcite compounds by means of combustion method. The results suggested that HT from using glycine as fuel is suitable for application requiring thermal endurance.

Karthikeyan and Manivannan in 2014 had reported the environmentally benign neem biodiesel synthesis using nano Zn-Mg-Al hydrotalcite as solid base catalysts. They

elucidated that the calcined nano hydrotalcite is an effective catalyst for the synthesis of biodiesel from neem oil.

Wang and He in 2014 studied the removal of fluoride from water by Ni-Al layered double hydrotalcite prepared by solvothermal method and found that the samples have a high sorption capacity at broad range pH.

Babakhani et al. in 2014 investigated the optical and thermal properties of Zn-Al layered double hydroxide nanocomposite intercalated with sodium dodecyl sulfate (SDS). They reported that the crystallinity of the LDH-SDS nanocomposites increased by increasing the amount of SDS.

In 2014, Valverde et al. prepared the V-Mg-Al catalyst from hydrotalcite for the oxidative dehydrogenation of propane. They found only pyrovanadate-containing catalysts active and selective to propene in propane oxidative dehydrogenation.

Feng et al. in 2015 studied the supported catalysts based on LDHs for catalytic oxidation and hydrogenation, general functionality and promising application prospects. They reviewed and summarized the recent progress in supported catalysts by using LDHs.

In 2015, Karthikeyan and Manivannan had reported the synthesis and catalytic activity of nano HT with different cations (Zn, Ni, Cu) for transesterification of vegetable oil. They found that the calcined nano HT has numerous advantages for transesterification of vegetable oil such as high catalytic activity, easy separation, recyclable, nontoxic and inexpensive catalysts.

Rashad and Someda in 2015 had synthesised Zn-Al LDHs and studied their applications in removal of technetium from aqueous solutions. The results showed that sorption of pertechnetate takes place from acidic solution of pH nearly 3 and the sorption on the surface of LDH may participate in the removal of technetium.

Degradation of PET-bottles to monohydroxyethyl terephthalate (MHT) using ethylene glycol and HT has been studied by Sharma et al. in 2015. The product could be easily separated from reaction mixture and the solvent and the catalyst could be reused.

Synthesis and characterization of hydrotalcite at different Mg-Al molar ratios, Wiyantokoa et al. in 2015 had conducted this study. They reported that chemical properties of prepared hydrotalcite are affected by molar composition.

Sahu in 2016 studied the eco-friendly grinding synthesis of double layered nano material and correlation between basicity, calcinations and catalytic activity in green synthesis of novel fused pyrimidines. This study reported a rapid and cost-effective synthesis of HT.

In 2017, Barik and Badamali had reported the LDH reinforced polymer bionanocomposites for packaging applications. They found that LDH based bionanocomposites possessed enhanced mechanical properties, good gas and moisture barrier properties which make these materials suitable for the packaging industry.

A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade, has been studied by Uddin, in 2017. He found that both natural and modified forms of the clay minerals have excellent feasibility in removing different toxic aquatic metal pollutants.

Bharali in 2017 had reported the synthesis, characterization and application of transition metal based LDHs. The results showed that introduction of transition metals in Mg-Al LDH greatly affected the adsorption efficiency of the LDH samples for removal of methyl orange from aqueous solution.

A green approach to the synthesis of a nano catalyst and the role of basicity, calcination, catalytic activity and aging in the green synthesis of 2-aryl benzimidazoles, benzothiazoles and benzoxazoles has been studied by Sahu in 2017. He reported that prepared HT could be used effectively in selective, eco-friendly and green synthesis for a variety of compounds and could be easily separable and recyclable.

Barbosa et al. in 2017 had reported the structural analysis of Mg-Al HTs modified with iron III obtained by hydroxide precipitation method. They found that the carbonated Mg-Al-Fe HT presented full inherent structural and morphological properties of anionic clay adsorbent materials and could be reused.

In 2017, Ayawei et al. studied the Mg-Fe LDH as a novel adsorbent for the removal of congo red. The results showed that the overall adsorption process is dependent on temperature and showed a feasible and favourable adsorption process.

Shekoohi et al. in 2017 had carried out the synthesis of some Mg-Co-Al type nano hydrotalcites and characterization. The increase in M^{2+}/M^{3+} ratio caused changes in the layered spacing and particles sizes became larger.

Lin et al. in 2017 studied the synthesis and optical properties of Mg-Al LDHs precursor powders. They concluded that all the Mg-Al LDH precursor powders contain only a single phase of $[Mg_{0.833}Al_{0.167}(OH)_2]$ $(CO_3)_{0.083}\cdot$ $(H_2O)_{0.75}$ but have broad and weak intensities of peaks.

Gupta et al. in 2017 had carried out the environmental benign synthesis of novel double layered nano catalyst and their catalytic activity in synthesis of 2-substituted benzoxazoles. They reported a green methodology for eco-friendly synthesis of a variety of substituted benzoxazoles under solvent free conditions.

In 2017, Yan et al. had studied the catalytic application of LDHs derived catalysts for the conversion of biomass-derived molecules. This review described an overview for the studies of LDH and its derived metal oxides (DMO) materials.

Hamlich et al. in 2017 had reported the calcined mussel shells doped with metal halides as a novel catalyst for the synthesis of benzimidazoles, benzoxazoles and benzothiazoles. The CMS/ZnCl2 had shown to be a highly efficient catalyst for the synthesis. This catalyst was natural, accessible, eco-friendly, inexpensive and recycled.

Ivankovic et al. in 2017 had reported a review of 12 principles of green chemistry in practice. Some of them are biocatalysis, catalysis, use of alternative renewable raw materials, alternative reaction media, alternative reaction conditions as well as new photocatalytic reactions.

In 2018, Sahu et al. had carried out the sustainable synthesis and characterization of Ni-Al containing double layered nano catalysts and their catalytic activity. They found that aging time affected the particle size of the nanomaterial and crystallinity was increased after hydrothermal aging.

Design, synthesis, ADME prediction and pharmacological evaluation of novel benzimidazole-1,2,3-triazole-sulfonamide hybrids as antimicrobial and antiproliferative agents, Al-blewi et al. in 2018 conducted this study. All compounds found were nonmutagenic and noncarcinogenic.

Grosu et al. in 2018 had reported the layered double hydroxides nanomaterials in biomedicine and (bio) sensing design. The LDHs materials had been found as good candidates for drug delivery, sunscreen products fabrication and active biomolecules incorporation due to their properties.

In 2018, Wang et al. prepared the dehydrogenation catalysts for synthesis of *o*-phenylphenol via Cu/Ni/Mg/Al hydrotalcite-like compounds as precursors. They found that the combination of Cu and Ni could greatly improve the stability and activities of the catalyst.

Bini and Monteforte in 2018 had reported the LDHs versatile and powerful hosts for different applications. Currently LDHs found application in many different fields from catalysis, agriculture, electrochemistry and nanomedicine.

Coumans et al. in 2018 studied the hydrotalcite-derived mixed oxides for the synthesis of a key vitamin A intermediate reducing waste. They reported that the catalyst could be readily recycled and reused, and any deposited organic species could be removed by oxidative regeneration without loss of performance.

In 2018, Qabaqous et al. had reported the removal of hexavalent chromium by ghassoul hydrotalcites membranes (GHTM). These membranes had a potential to find out an application for the economic treatment of wastewater containing toxic compounds.

Saikia and Goswamee in 2018 had studied the effect of strength of bases and temperature on the synthesis of Zn-Al LDHs by a non-aqueous 'soft chemical' sol-gel method and formation of high surface area mesoporous $ZnAl_2O_4$ spinel. They found that both temperature as well as the strength of bases affected the synthesis of Zn-Al LDH. $ZnAl_2O_4$ spinel formed showed application as important advanced materials like catalyst and catalyst support, ceramic material, photocatalyst, optical coating, high temperature ceramic material.

Bestianini et al. in 2018 had carried out a study on the caffeic acid-LDH hybrid, a new raw material for cosmetic applications. The results showed that Zn-Al-CAF possessed an increased bioavailability compared with the neat caffeic acid. The intercalation technology could greatly increase the use of caffeic acid in the cosmetic market.

In 2018, Benicioa et al. had reported LDHs as hosting matrices for storage and slow release of phosphate analysed by stirred-flow method. Among the LDHs obtained, Mg_2Al-LDH-P presented the highest amount of P and LDHs-P showed a gradual P release profile and Mg_2Al-LDH-P presented a slower release than the other materials.

Yan et al. in 2018 studied the research progress of Ni-Mn LDHs for supercapacitors. They reported that the asymmetric SCs based on Ni-Mn LDHs electrodes showed high energy densities with wide working voltages and might be an ideal precursor for the preparation of ternary metal oxides such as NiO and MnOX.

Laine et al. in 2018 had carried out a study on tuning the nature of the anion in hydrated LDHs for H_2 production under ionizing radiation. They found that the behaviour of LDHs under ionizing radiation mainly controlled by the nature of the anion and H_2 production could be minimized when nitrate anions present in the interlamellar space.

In 2018, Afi et al. had reported the LDHs as an efficient heterogeneous catalyst for the cyanosilylation of aromatic aldehydes. Mg-Al-Cu LDH found to be a good heterogeneous catalyst with electron-withdrawing and releasing groups under mild conditions.

Xiao et al. in 2018 studied the tailoring morphology of Co-Ni LDH via different surfactants for high-performance supercapacitors. The results showed that the morphology modification by the surfactant enhanced the electrochemical performance in Co-Ni LDH electrode materials.

In 2018, Nguyen et al. had reported the porous metal oxides derived from Cu-Al LDH as an efficient heterogeneous catalyst for the Friedel-Crafts alkylation of indole with benzaldehydes under microwave irradiation. They found that the mixed metal oxides (MMO) developed as inexpensive and non-toxic, recyclable and showed high yields within short reaction times.

de Marco et al. in 2018 had carried out a study on the evolution of green chemistry and its multidimensional impacts. They found that the industries needed to visualize the economic viability of applying green chemistry to their processes.

In 2019, Ali et al. had reported the environmental chemistry and ecotoxicology of hazardous heavy metals, environmental persistence, toxicity, and bioaccumulation. Heavy metals are considered hazardous due to these three characteristics: persistence, bioaccumulation, and toxicity (PBT).

Cheng et al. in 2019 have synthesised a novel antimicrobial composite Zn-Al-hydrotalcite with *p*-hydroxybenzoic acid (PHBA) intercalation and its possible application as a food

packaging material. The resulting sample demonstrated slow and sustained release characteristics for PHBA anions as a food simulant, thus proving its applicability for antimicrobial properties in packaging materials.

Liu et al. in 2019 had carried out a study on the enlarged interlayer spacing in Co-Mn LDH guiding transformation to layered structure for high supercapacitance. Co-Mn-LDH provided a solid basis of manipulating the interlayer spacing and crystal structure for effectively enhancing the supercapacitance.

Haraldy et al. in 2019 had reported the fabrication of Mg-Zn-Al HT and its application for Pb^{2+} removal. They found that the molar ratio variation of Mg-Zn-Al HT increased the positive charge of Mg-Zn-Al. The adsorption electiveness of Pb^{2+} also increased by calcination.

In 2019, Li et al. had synthesised the ternary Ni-Fe-Zr LDHs, a highly efficient catalyst for the oxygen evolution reaction (OER). These nanosheets provided effective paths for the diffusion and adsorption of electrolytes and gas products in the OER process.

So, literature study shows that hydrotalcite-type anionic clays have a number of applications in various fields. They are effectively used as adsorbents, green catalyst, PET degradation materials. They are also used in the pharmaceutical industry, cosmetics, agriculture, drug delivery, food packaging. These all applications show the importance of working with hydrotalcite-type anionic clays.

Research Gap Identification

Although a large number of research groups from all over the world synthesized hydrotalcite-type anionic clays and studied their properties, there are many fields which are yet to be discovered. Also, hydrotalcite-type anionic clays have some interesting properties different from conventional base catalysts, which attracted focus of this research in this area. In addition to this, applications of synthesized hydrotalcite-type anionic clays for catalysis need much more attention. So, in the present study we would use hydrotalcite-type anionic clays to explore its catalytic activity for the synthesis of piperidine heterocyclic compounds as well as for their recycling efficiency.

Objectives

In the light of above discussions, the objectives of present study are as follows:

1. To synthesize Ni, Zn, Mg, Li, Ca, Co, Cu, Mn, Pb and Cd based hydrotalcite-type anionic clays.
2. To characterize the synthesized hydrotalcite-type anionic clays by using different characterization techniques like FT-IR, XRD and SEM-EDX.
3. To evaluate the applications of hydrotalcite-type anionic clays in catalysis.

Proposed Methodology

In the literature, a number of methods of synthesis are reported for hydrotalcite-type anionic clays. In present study, we propose to use the co-precipitation method.

Materials

Nickel nitrate, zinc nitrate, magnesium nitrate, lithium nitrate, calcium nitrate, cobalt nitrate, copper nitrate, manganese nitrate, lead nitrate, cadmium nitrate, aluminium nitrate, sodium hydroxide, sodium carbonate and ethanol of high purity will be used.

Methods

Preparation of Hydrotalcite Type Anionic Clays

For the preparation of hydrotalcite-type anionic clays, a fixed amount of divalent and trivalent salts will be mixed with a fixed volume of solution of NaOH and Na_2CO_3 until the pH will be adjusted to a fixed range. Afterwards, a slurry will be observed with crystallized particles at this pH, which will be further stirred under heating. Then the slurry will be cooled and the precipitate will be filtered followed by washing with deionized water. The wet solid will be dried in an air oven (Sahu et al., 2018).

Characterization of Synthesized Hydrotalcite Type Anionic Clays

Prepared hydrotalcite-type anionic clays will be characterized by using FT-IR spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM) with EDX.

Applications of HT- like materials

In this study, experiments will be performed to evaluate the catalytic activity of the synthesized hydrotalcite-type anionic clays by the synthesis of piperidine heterocyclic compounds and degradation of plastic.

Thesis Outline

CHAPTER 1 (Introduction): This chapter will contain the brief introduction regarding clays, catalyst, hydrotalcite-type anionic clays, methods of synthesis.

CHAPTER 2 (Literature Review): This chapter will deal with intense literature survey of synthetic methods and applications of hydrotalcite-type anionic clays.

CHAPTER 3 (Materials and Methods): It includes the experimental details about the material used, methods of synthesis, characterization techniques and applications of synthesised hydrotalcite-type anionic clays.

CHAPTER 4 (Results and Discussion): This chapter will include detailed discussion on results of present work which includes the key points and various aspects of synthesis, characterization and applications of hydrotalcite-type anionic clays.

CHAPTER 5 (Summary and Conclusions): This chapter will summarise and correlate all the above-mentioned chapters in lucid manner.

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